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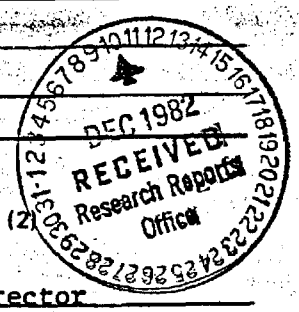


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Correlation and collective modes have been studied for systems with quite localized valence or conduction bands. In particular this research has been concerned with localized electron-hole states and how they contribute with other excitations to the dynamical response of the system. Important aspects studied have been the effects of exciton or exciton-like states on superconducting properties, electron energy loss spectra and optical spectra. Initially the system studied has been CuCl for which a tight-binding model was used. The results show that strong effects due to localized excitations

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of d-band electrons greatly affect the dynamical response and the effective electron interaction. The exciton resonance in the dynamical response is necessary to obtain the appropriate attractive effective electron interaction for superconductivity. Models have also been set up to relate the dynamical response including local field effects to the superconducting transition temperature and gap function. The strong localization effects also will affect the loss spectra and optical spectra. Further calculations are planned for CuCl and also for CdS and $Cu_2O$.

Table of Contents

## I. Research Objectives

The overall objective of this work is to study correlation and collective modes for systems with quite localized valence or conduction bands. For these systems one must consider the effects of localized excitations and collective modes to understand large scale correlated states such as superconductivity or the interaction of the system with optical or electronic probes. In certain cases, such as for narrow-band insulators, one must consider these effects to understand even ground state properties. In particular this research has been concerned with localized electron-hole states and excitonic modes and how they contribute with other excitations to the dynamical response of the system.

The effect of strongly localized excitations on the superconducting properties of a material can be significant. We are most concerned with the effect on the superconducting mechanism itself. For systems such as oxidized Cu or CuCl, there are some experimental indications that the usual phonon-coupling mechanism is augmented or even dominated by an exciton-coupling mechanism. We have developed some models to describe the excitation structure in terms of excitons alone and with these have studied local field effects on the dynamical response. Our objective is to discover whether excitons can cause an attractive response.

The effects of localized excitations on the response to optical or electronic probes is known to be significant. Our exciton models have already successfully explained the optical absorption due to intrinsic excitons in several materials. Our objective here is to provide a detailed description of the effects of local field corrections and umklapp scattering terms on the dielectric response of these materials. Using the same models to describe the collective modes, and dynamical response of a system, such as superconductivity and the response to optical or electronic probes, we are arriving at a

consistent description of these systems.

Eventually our models will lead to a clear picture of the superconducting state in narrow band materials and what conditions will lead to optimized properties. Also we will have a better understanding of the electronic excitation structure of these systems and of the structure of the optical absorption and electron energy loss spectra. In addition we are developing methods for describing the effect of correlations between metal and adsorbate valence electrons on the bonding and vibrational excitations of metal-adsorbate systems. We will discuss these calculations further below.

## II. Investigations of Electronic Structure in Narrow Band Materials

We have developed several theoretical methods and models for dealing with the electronic structure and properties of narrow band materials. Among these are:

1. Tight-binding models - These are models which describe the d- and s-valence band electronic structure of materials. They can be used to give the density of states of transition metals, alloys and compounds.

2. Surface and grain boundary segregation models - Using the tight-binding density of states and minimizing the system free energy, one can obtain the surface and grain boundary composition. We have extended this model to the surface segregation of ternary alloys and are extending it to include d-band effects in grain boundary segregation. We have also developed a model for the diffusion of a non-uniform implant profile in the presence of a surface. The model shows that considerable nonequilibrium implant surface segregation can occur under certain conditions even if there is no equilibrium surface segregation.

3. Excitonic Superconductivity Models - We have used the tight-binding model to develop a model for excitonic effects on the attractive effective electron-electron coupling which includes local field effects and the effects of valence and conduction band structure. We have also developed a model for the superconducting transition temperature and gap equation which includes local field and excitonic effects.

4. Cluster calculation methods - We have extensive experience with ab-initio Hartree-Fock and linear-combination-of-atomic orbitals Xα (LCAOXα) molecular cluster methods. These methods give a detailed description of local electronic structure and they are self-consistent so that they describe the rearrangement of the electrons even for changes in complicated geometries. In

particular the methods are useful for defects in the bulk or at surfaces or boundaries, for studying certain localized catalytic and adsorption processes, and for systems of complicated local geometries which are likely to have localized electronic states. We have extended the methods to long range systems by applying embedding models which include the dominant effects of the environment on the cluster. Our recent calculations are for $H_2O$ adsorbed on Cu surfaces where we explore the correlation of Cu d and s electrons with O p and s electrons to produce surface-adsorbate bonds. Our calculations show that for certain adsorbate geometries significant differences appear in the $H_2O$ bond distances and potential energy surfaces as compared to free $H_2O$.

Some of our papers and presentations in the past two years in the general area of properties of transitions metals or narrow band materials are:

"Optical Constants of $TiO_2$," Handbook of Optical Constants (Pergamon, New York, 1982).

"Surface Segregation in Ternary Alloys," 42nd Physical Electronics Conference, Atlanta, Ga. (1982).

"Exciton Coupling and the Effective Electron Interaction in Narrow Band Materials," A.P.S. March Meeting, Los Angeles (1983).

"Local Field Effects on Exciton Coupling in CuCl and CdS under Pressure," High Pressure in Science and Technology (Elsevier, Ner Work, 1984).

"Local Field Effects Due to Excitons and the Superconducting Coupling Constant," A.P.S. March Meeting, Detroit (1984).

"The Diffusion of Implanted Ions near Surfaces and Grain Boundaries," A.P.S. March Meeting, Detroit (1984).

"Electronic Structure Calculations of Water on a Copper Surface," 44th Physical Electronics Conference (June, 1984).

"Exciton Mechanism of Superconductivity in CuCl," to be submitted.

"Diffusion and Non-Equilibrium Surface Segregation of Implanted Ions," to be submitted.

## III. Local Field Effects and the Superconducting Transition Temperature

The general success of the Bardeen, Cooper, and Schrieffer[1] (BCS) model of superconductivity, where the pairing interaction is taken to be a constant in a narrow region near the Fermi surface, obscures the fact that the interaction is really frequency and momentum dependent. In fact the pairing arises from an effective interaction which depends on the dielectric response and, in general, includes local field effects. Local field effects are critical in explaining high transition temperatures in certain superconductors.[2] The inclusion of exchange interactions, which give rise to exciton effects and improve the description of the excitation spectrum may, also contribute significantly to the transition temperature for certain cases.

The purpose of this section is to describe a model for a superconducting state in terms of Coulomb interactions alone. Thus the dielectric response of the surrounding medium must be included explicitly to obtain an attractive interaction between electrons. The dielectric response is frequency dependent and contains exchange interactions so that one may evaluate the strength of both the exciton and plasmon pairing mechanisms. The following description in terms of Bloch states is new, and we therefore develop the method in some detail.

The paired electrons are described in terms of an anomalous Green's function

$$F_{nn'}(\vec{p},i\omega_p) = -\int_0^{1/T} d\tau\, e^{i\omega_p \tau} \langle T_\tau\, C_{n\vec{p}\uparrow}(\tau) C_{n'\vec{p}\downarrow}(0)\rangle, \qquad (1)$$

where n and n' refer to Bloch states, T is the temperature, and Eq. (1) is in the temperature Green's function formulation.[3] The bracketed term is $\tau$-ordered with the bra and ket states differing by occupation of the pair state

$(n\vec{p}\uparrow, n'\vec{p}\downarrow)$ so that the bracketed term is a pair propagator. The quantity $\tau$ is an imaginary time, and thus Eq. (1) involves the analytic continuation of the pair propagator to the imaginary axis.

The anomalous Green's function can be expanded in a manner similar to the usual one particle Green's function giving

$$F_{nn'}(\vec{p}, i\omega_p) = \frac{1}{i\omega_p - \varepsilon_{n\vec{p}}} \frac{1}{i\omega_p + \varepsilon_{n'\vec{p}}} \tag{2}$$

$$T_c \sum_{\substack{n_3, n_4 \\ \vec{q}, \omega_q}} \Gamma_{nn' n_3 n_4}(\vec{p}, \vec{q}; i\omega_p - i\omega_q) \; F_{n_3 n_4}(\vec{q}, i\omega_q)$$

where the terms with $\varepsilon_{n\vec{p}}$ are one-particle non-interacting Green's functions in the Bloch basis and $\Gamma$ is the electron vertex function. The equation is evaluated at the critical temperature $T_C$ so that $\varepsilon_{n\vec{p}}$ is the energy spectrum for the normal state.

The quantity $\Gamma$ can be approximated as

$$\underline{\Gamma}^L(\vec{p}, \vec{q}; i\omega_p) = \underline{\varepsilon}^{-1}(\vec{p}, \vec{q}; i\omega_p) \; \underline{V}(\vec{p}, \vec{q}) \tag{3}$$

where V is the Coulomb interaction matrix in the Bloch basis. In this approximation $\Gamma$ is just the screened interaction and includes local field effects. If Eq. (3) is placed in Eq. (2) and the system of equations solved self-consistently for $F_{nn'}$, we have a solution in the Gorkov-Ladder Approximation.[4] However, before solving Eq. (3) it is necessary to simplify further. We are most interested in the $n = n'$ element of F, and it is a good approximation in many cases to assume that we can neglect $n_3 \neq n_4$ terms in Eq. (2). With this assumption we have a diagonal approximation for F which still contains local field effects via $\Gamma^L$.

We can now reformulate our superconductor equations in a form similar to the BCS equations. To do this we define a gap function[4]

$$\Delta_n(\vec{p}) \equiv 2|\varepsilon_{n\vec{p}}| \int_0^\infty \frac{d\omega'}{\pi} \operatorname{Im} F_{nn}^R(\vec{p},\omega') \tag{4}$$

in terms of the imaginary part of the retarded anomalous Green's function $F^R$. We obtain $F^R$ by continuing analytically, $i\omega_p \to \omega + i0^+$, in Eq. (2). We can convert the $\sum_{\omega_q}$ to a contour integral in the usual manner.[3] If we assume a weakly coupled superconductor, $F^R$ has approximately a quasi-particle spectrum so that

$$\operatorname{Im} F_{nn}^R(\vec{q},\omega) = \pi\Delta_n(\vec{q}) \frac{\delta(\omega-|\varepsilon_{n\vec{q}}|)}{2\varepsilon_{n\vec{q}}} . \tag{5}$$

As a result we obtain

$$\Delta_n(\vec{p}) = -\int_\varepsilon^\infty \frac{d\omega'}{2\omega'} \tanh\frac{\omega'}{2T_c} \sum_{n_3} \Delta_{n_3}(\omega') \times K_{nn_3}(\vec{p},\omega') \tag{6}$$

where we have used $\vec{q} = \vec{q}(\omega')$ as a result of Eq. (5). The kernel K is a generalization of the usual homogeneous form (see Ref. 4). The Fermi energy $\varepsilon_F$ is the lower bound of the integral because $\varepsilon_{n\vec{q}}$ is assumed measured relative to $\varepsilon_F$.

If we use the procedure of Zubarev,[5] which is valid for weakly coupled superconductors, we may obtain an expression for $T_c$ which is quite similar to the BCS expression. To do this it is convenient to assume

$$|\vec{p}| = (2m^*(\omega+\varepsilon_f))^{1/2} .$$

The expression for $T_c$ is then

$$T_c = 1.134\ \varepsilon_F \exp\left[\frac{1}{\beta_{no}} + \int_{-1}^{\infty} \frac{dx}{2|x|} \sum_{n_3} \frac{\Delta_{n_3}(x)}{\Delta_n(o)} K_{nn_3}(o,x)/\beta_{no} - \theta(1-|x|)\right], \tag{7}$$

$$x \equiv \omega/\varepsilon_F ,$$

where

$$\beta_{no} \equiv \sum_{n_3} \frac{\Delta_{n_3}(o)}{\Delta_n(o)} K_{n_3 n_3}(o,o)$$

The corresponding equation for $\phi_n(x) = \Delta_n(x)/\Delta_n(0)$ in the Zubarev approximation, which allows us to neglect the $T_c$ dependence, is

$$\phi_n(x) = K_{n,n}(x,0)/K_{nn}(0,0) - \int_{-1}^{\infty} \frac{dx'}{2|x'|} \sum_{n_3} \frac{\Delta_{n_3}(x')}{\Delta_n(o)} \left[K_{nn_3}(x,x') - \frac{K_{nn}(x,o)}{K_{nn}(o,o)} K_{nn_3}(o,x)\right] \tag{8}$$

We can treat Eq. (8) as a linear integral equation and solve for $\phi_n(x)$ and then find $T_c$ using Eq. (7). Equations (7) and (8) are new results for inhomogeneous periodic systems which reduce to the previously found homogeneous equations.[4]

## IV. Tight Binding Calculations of the Electronic Response

The difficulty of the calculation has impeded the inclusion of local field effects and non-local exchange in the evaluation of the dynamical electronic response. One must construct and then invert a matrix for each momentum transfer and frequency to obtain the dielectric matrix $\underline{\underline{\varepsilon}}^{-1}$ in Eq. (3) above, and the calculation of $\Delta$ involves an integral over momentum and frequency. This is the typical task one faces, and thus few calculations of dynamical properties which include local field effects and exchange have been done. We overcome this calculational difficulty by choosing a simple model which still takes into account electronic localization and exchange.

Our tight binding model is based on a model developed by Prakash and Joshi[6] and extended by Hanke to the lattice dynamics of Pd and Ni.[7] One assumes that the band structure of the system is adequately described by a non-interacting band model. Then one connects the high-symmetry points in the band structure according to compatibility and which atomic level they represent by symmetry (for example $\Gamma_{12}$ connects with $L_3$ in FCC structures because both states represent $d_{m=2}$). The bands are then described as parabolas with an effective mass assigned to give them the optimal shape. The Bloch states in the tight-binding formulation are just

$$\Psi_\nu^{\vec{k}}(\vec{r}) = \frac{1}{N_{\frac{1}{2}}} \sum_{\ell} e^{i\vec{k}\cdot\vec{R}_\ell} u_\nu(\vec{r}-\vec{R}_\ell) \quad ,$$

where $u_\nu$ is the appropriate atomic wave function. Although these approximations are fairly extreme, the model dielectric screening, when used in calculations of the phonon dispersion for Pd and Ni, gives good results.[7]

The simplest band model for the transition metal system of interest here is an s-d band model. We can augment this model by assuming the d bands are

hybridized with, for example, O or Cl p states in the case of the oxide or chloride. In the s-d band model, the dielectric matrix is

$$\underline{\underline{\varepsilon}} = \underline{\underline{1}} - \underline{\underline{\varepsilon}}_{ss} - \underline{\underline{\varepsilon}}_{sd} - \underline{\underline{\varepsilon}}_{ds} - \underline{\underline{\varepsilon}}_{dd} \cdot \tag{9}$$

When d-d intraband terms contribute, our calculations[8] indicate that $\underline{\underline{\varepsilon}}_{dd}$ dominates in Eq. (9). Hanke also found this to be the case for Pd and Ni.[7] We can then use a zero overlap approximation where we neglect intersite overlap. The Coulomb and exchange interaction matrices then take the simple form

$$V_{m\ell,m'\ell'}(q) = \sum_{G} A^{*}_{m\ell}(\vec{q}+\vec{G})\ V(\vec{q}+\vec{G})\ A_{m'\ell'}(\vec{q}+\vec{G}) \tag{10}$$

$$V^{x}_{m\ell,m'\ell'}(q) = \sum_{G} A^{*}_{m\ell}(\vec{G})\ V_{\vec{G}}\ A_{m'\ell'}(G)$$

where

$m,m'$ : unoccupied d states

$\ell,\ell'$ : occupied d states

and

$$V_{\vec{q}} = \frac{4\pi e^2}{q^2}$$

The overlap matrix $A_{m\ell}$ is

$$A_{m\ell}(\vec{q}+\vec{G}) = \int U^{*}_{m}(\vec{r})\ e^{i(\vec{q}+\vec{G})\cdot\vec{r}}\ U_{\ell}(\vec{r})\,d\vec{r} \quad .$$

The zero-overlap approximation in Eq. (10) allows us to include exchange effects just as easily as Coulomb effects, which is not the case when overlaps are included.[9]

It is most convenient to use the notation of Hanke and Sham to construct $\underline{\varepsilon}^{-1}$.[9] However in the present tight-binding case, the matrix elements are over the band states themselves rather than just the local orbital basis. Then

$$\underline{\varepsilon}^{-1}(\vec{p},\vec{q};\omega) = \sum_{\substack{\vec{R}_a,\\ \vec{R}_b}} e^{-i\vec{p}\cdot(\vec{R}_a-\vec{R}_b)} \left[ \delta_{\vec{R}_a,\vec{R}_b} - \underline{S}(q,\omega;\vec{R}_a,\vec{R}_b) \right] \tag{11}$$

where

$$\underline{S} = \underline{N}^o[\underline{1} - (\underline{V} - \tfrac{1}{2}\underline{V}^x)\ \underline{N}^o]^{-1} \quad ,$$

and the non-interacting polarizability $\underline{N}^o$ is given in Eq. (2.10) of Ref. 9 with all expansion coefficients C set equal to one. We can use Eq. (11) in Eq. (3) to find $\Gamma^L$ and then find $\Delta_n$ and $T_c$.

Our calculation for CuCl using this model have recently been published in High Pressure in Science and Technology. The paper is reproduced in the Appendix.

## V. Probes of Other Collective Phenomena

In addition to superconductivity, our study of the dynamical dielectric response opens the door to investigations of other collective phenomena. Among these are plasmons and a variety of electronic excitation processes of which the exciton is one. Our tight-binding model also makes it a good deal easier to study these processes from a dielectric response framework. We connect some of these phenomena with electronic and optical processes which probe them in this section.

Two processes that are closely related in that they both depend on the dynamical response of a system in a similar way are electron energy loss spectroscopy (EELS) and optical absorption. For narrow bands these processes exhibit behavior, which workers are just now beginning to understand, related to the presence of strong local field effects. Since EELS and optical absorption spectroscopy are used extensively as probes of the ground and excited electronic structure of a system, it is important to understand fully their features.

### A. Optical Absorption Spectra

The response to an electromagnetic field is in terms of a macroscopic dielectric function[10]

$$\varepsilon(\omega) = \lim_{q \to o} \frac{1}{\varepsilon^{-1}(\vec{q},\vec{q};\omega)} \tag{13}$$

The optical absorption is given by $\mathrm{Im}\{\varepsilon(\omega)\}$. When local field effects are important,

$$\varepsilon^{-1}(\vec{q},\vec{q};\omega) \neq \frac{1}{\varepsilon(\vec{q},\vec{q};\omega)} \quad ,$$

and one must invert the matrix $\varepsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}';\omega)$. It is a straightforward matter to implement these calculations from the tight-binding treatment outlined in the last section.

Hanke and Sham have shown that large contributions from local field effects and from exchange interactions leading to exciton effects must be included to obtain agreement with the experimental optical spectra of diamond[9] and silicon.[11] These effects involve a significant increase of the low energy side of the absorption peak when local field effects and exchange effects are included.

Recently, calculations for Mg[12] have shown that these effects can be quite important in polyvalent metals. These calculations indicate that the principal interband optical process creates an excitonic effect which closely resembles the 3s-3p excitation structure in the Mg atom. In this case, theories which assume the electron and hole are dynamically independent are seriously in error. A zero-overlap approximation for the Mg electron-hole interaction,[12] which is quite similar to the approximation we use, gives a calculated threshold peak in good agreement with the experimental peak. Similar peaks, which change position smoothly with concentration, are seen in alloy systems.[13] For example, in Mg-Li the threshold peak moves to higher energy as the Li concentration is increased.[13] The lowering in peak intensity with increasing Li concentration is due to the dependence on the density of Mg sites, and the smooth shift in peak energy reflects the effectiveness of electron-hole interaction screening for different alloy compositions. Thus a polyvalent metal which is nominally nearly free electron-like with a high density of electrons in the stationary states near the Brillouin zone face exhibits strong electron-hole correlations. Such effects should certainly be seen for transition metals with more localized valence bands.

B. Electron Energy Loss Spectra

The EELS may be interpreted in terms of energy loss suffered by fast electrons,[14] since the primary energies of concern to us will be 100 eV or more. In this energy regime, $E_p >> \varepsilon_F$ where $\varepsilon_F$ is the Fermi energy so that the Born approximation is valid and scattering is described in terms of the response of the correlated electron system. Then the probability per unit time per unit solid angle that the electron will be scattered while suffering an energy loss $\omega$ is

$$P(\gamma,\omega) = F(\gamma,\omega)\ \mathrm{Im}\{\varepsilon^{-1}(\vec{q},\vec{q};\omega)\}\ , \qquad (14)$$

where $F(\gamma,\omega)$ is a kinematic factor depending on the geometry of the scattering event and the initial momentum $P_c$, and $\gamma$ is the solid angle depending on the scattering angle, $\cos^{-1}(\vec{P}_e,\vec{P}_e+\vec{q})$. Upon comparing Eq. (14) with Eq. (13), we see that EELS involves the same response function as optical absorption, but in the former case there is a finite momentum transfer.

The main components of EEL spectra above 5 eV or so are surface and bulk plasmon peaks and interband transition peaks. The plasmon peaks are the most prominent features for titanium metal,[15] but interband transitions increase in prominence as the 3d shell fills up owing to the narrowing of the d band. Even though the plasmon peaks have been observed for many years, a full explanation of their energy positions has never been given. The role of the tightly-bound d electrons, in particular, is uncertain. Moreover, the positions of the plasmon peaks evidently change depending on whether reflection[15] or transmission[16] EELS is used. A possible explanation is that the higher primary energy transmission experiments involve greater momentum transfer to the plasmons than do the reflection experiments so that dispersion

changes the plasmon energy. However no studies have been done on plasmon dispersion in transition metals. Most likely local field effects and electron-hole interactions are important contributions to the plasmon and interband loss structures of transition metal systems, and the tight-binding approach will allow the calculation of the trends in these contributions across the transition metal series.

## VI. Localized Bonding States for Water Adsorbed on Copper

We have recently used another approach to describe the local electronic configurations and the correlation which comes about via bonding in adsorbate-metal surface systems. We have used linear combination of atomic orbitals $X\alpha$[17] (LCAO$X\alpha$) cluster calculations to study $H_2O$ monomers on a Cu surface. Quite recently experimentalists have isolated these monomers on a metal surface for the first time and studied them with high resolution EELS.[18] This technique explores a much lower energy range than the EELS discussed in the last section, and in this application is used to investigate surface vibrations. An explosion of interest in this technique has occurred in the last few years because it gives so much information about bonding of adsorbates, site configuration and location, and even about surface phase transitions that can occur as a function of temperature or as different species are co-adsorbed. A theoretical model which could successfully describe the spectra would be quite valuable not only in contributing to a basic understanding of surface processes but also in clarifying many catalytic and corrosion mechanisms.

Our calculations for small clusters of Cu and $H_2O$ give results for the binding energy, basic bonding mechanism and orientation of the $H_2O$ which are in agreement with results which can be inferred from the EELS and other experimental data.[18] There is also good qualitative agreement between our results and the experimental vibration frequencies. We see a bright outlook for further calculations of this type. An extended abstract appears in the Appendix for a paper on this work which has been accepted for the 44th Physical Electronics Conference.

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# LOCAL FIELD EFFECTS ON EXCITON COUPLING IN CuCl AND CdS UNDER PRESSURE*

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ABSTRACT

The role of exciton coupling in the interactions of electrons in the valence and conduction bands of CuCl and CdS is studied. In particular, the off-diagonal elements of the inverse dielectric matrix and their association with local field effects via umklapp processes are investigated. Calculations on CuCl show that the local field contribution to the effective electron interaction is quite prominent and that the exciton plays an important role in determining the attractive region of the effective electron interaction. The effect on the attractive region of changes in the conduction band under pressure and the introduction of a number of free carriers is also studied.

Over the past fifteen years there have been several attempts to describe and to find experimentally an exciton mechanism of superconductivity. The reason for this interest is the enormous potential which would accompany a superconductor with a temperature significantly higher than the present maximum of around 25°K. About ten years ago, Allender, Bardeen and Bray[1](ABB) came up with a detailed model for an exciton mechanism of superconductivity based on a perturbation theory calculation for a narrow gap semiconductor in contact with a metal. They found a significant increase of the transition temperature over that for the phonon mechanism alone. In a rebuttal, however, Inkson and Anderson [2] showed that second-order perturbation theory was inadequate to describe the exciton response and that for silicon, at least, there was no enhancement of the critical temperature due to excitons. More recently, observations of near perfect diamagnetism in CuCl and CdS under pressure [3] which might indicate a superconducting-like state at temperatures up to 300°K have revived interest in this phenomenon. Quite recently, calculations by Collins et al [4] have shown that an exciton-mediated high temperature superconducting state can exist in CuCl if one assumes an appropriate exciton-electron interaction and density of free carriers.

A critical element in any exciton model of superconductivity is the nature of the effective electron interaction. Because of the difficulty in doing the calculation, nobody has come up with a detailed study of the effective interaction appropriate for a system with narrow valence bands such as CuCl or CdS. We show here that such a calculation is possible using a tight-binding approach. In this first calculation, we use a non-interacting band model [5] which Hanke [6] has used successfully to describe the contribution of static screening to the lattice dynamics of Pd and Ni. Hanke has shown [6,7] that the dielectric matrix $\varepsilon$ can be reformulated in the tight-binding model so that the inverse matrix $\varepsilon^{-1}$ can be found in the compact tight-binding basis. Unfortunately, when plane wave-like states are important, as they are for CuCl, one cannot convert to the tight-binding basis and must invert $\varepsilon$ in the basis of reciprocal lattice vectors so that a much larger matrix results. The equation one must solve for a system with d and s-like valence and conduction bands is

$$\varepsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) = [\delta_{\vec{G},\vec{G}'} - \varepsilon_{ss}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) - \varepsilon_{dd}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) - \varepsilon_{ds}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) - \varepsilon_{sd}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega)]^{-1} \quad (1)$$

where $\vec{q}$ is the momentum transfer, $\vec{G}$ is a reciprocal lattice vector and $\omega$ is the frequency.

The terms in Eq. (1) all have similar structures and one has, for example, for the d-s interband term

$$\varepsilon_{ds}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) = \frac{1}{\Omega_o} v(\vec{q}+\vec{G}) \sum_{m\vec{k}\vec{H}} N_m^{ds}(\vec{q}+\vec{H},\vec{k};\omega) A_m^{ds}(\vec{k}+\vec{H}-\vec{G}) A_m^{ds}(\vec{k}+\vec{H}-\vec{G})^* \quad . \qquad (2)$$

Here, $v(\vec{q}+\vec{G})$ is the bare coulomb interaction, $N_m^{ds}$ is a polarization whose static form is given by

$$N_m^{ds}(\vec{q},\omega) = \sum_{\vec{k}} \left[ \frac{f(d_m,\vec{k})(1-f(s,\vec{k}+\vec{q}))}{\omega+E(d_m,\vec{k})-E(s,\vec{k}+\vec{q})+i0^+} - \frac{f(d_m,\vec{k}+\vec{q})(1-f(s,\vec{k}))}{\omega+E(d_m,\vec{k})-E(s,\vec{k}+\vec{q})-i0^+} \right] \qquad (3)$$

and the d-s overlap matrix element is

$$A_m^{ds}(\vec{k}+\vec{H}-\vec{G}) = \left(\frac{1}{\Omega_o}\right)^{1/2} \int_{N\Omega_o} u_{dm}^*(\vec{r}) e^{i(\vec{k}+\vec{H}-\vec{G})\cdot\vec{r}} \, d\vec{r} \quad . \qquad (4)$$

In Eq. (3) f is the Fermi occupation number, $E(d,\vec{k})$ is d band energy and $\omega$ is the frequency. We assume a plane wave for the s state in Eq. (4) and the d state $u_{dm}$ is just the Cu atomic d wave function.

TABLE I. Band structure parameters for CuCl at equilibrium pressure

| lattice parameter | 10.215 a.u. | energy levels at high symmetry points (a.u.) | |
|---|---|---|---|
| crystal structure | zincblende | | |
| effective masses (in units of $m_e$): | | $\Gamma_{12}$ | -.051 |
| $m\{\Gamma_{12} - (X_1,X_2)\}$ | 20 | $\Gamma_{15}(2)$ | 0.0 |
| $m\{\Gamma_{15}(2) - (X_3,X_5)\}$ | 5.1 | $\Gamma_1(2)$ | .125 |
| $m\{\Gamma_1(2) - X_1(3)\}$ | 1.28 | $\Gamma_{15}(3)$ | .393 |
| $m\{\Gamma_{15}(3) - X_3(3)\}$ | 1.2 | $X_1(2), X_2$ | -.041 |
| | | $X_5(2), X_3(2)$ | -.037 |
| | | $X_3(3)$ | .236 |
| | | $X_1(3)$ | .273 |

We have chosen the equilibrium band structure of Zunger and Cohen [8] as the starting point for this calculation, except that we have adjusted the band gap to be identical with the experimental gap. The Zunger and Cohen calculation and several others show the topmost valence band to be mostly Cu3d and the bottom of the conduction band to be Cu4s. However, the lowest X point is the conduction band is mainly of 3d character. To maintain pure d and s character in the conduction bands, we therefore assume that d-like $\Gamma_{15}(3)$ connects with $X_3(3)$ while s-like $\Gamma_1(2)$ connects with $X_1(3)$. We use an effective mass approximation to connect the high symmetry points at X and $\Gamma$ and assume the bands are isotropic. The equilibrium band structure parameters for this approach are given in Table I. For the Cu3d and Cl3p

states, we use atomic wavefunctions and assume that they are localized enough so that there is no interatomic overlap between these states. For the conduction band s states, we use single plane waves orthogonalized to the valence states. The orthogonalization is quite important, especially for the behavior at small q. We retain the Cu3d-Cl3p mixing at the top of the valence band found both theoretically and experimentally by using a mixing of 25% Cl3p and 75% Cu3d for the d-like valence bonding state and a 75% Cl, 25% Cu mixing for the conduction band anti-bonding state.

The inclusion of exchange in our model is a difficult problem owing to the non-local nature of the exchange interaction. For these calculations we have chosen a simple local form for the exchange interaction by replacing $v(\vec{q})$ by

$$v(\vec{q}) \; [1-g(\vec{q})]$$
$$f(\vec{q}) = Cg_H(\vec{q})$$

where $g_H(\vec{q})$ is the Hubbard exchange factor [9] formulated for the interacting electron gas. The constant C is adjustable, and we vary it to obtain the correct fundamental exciton binding energy. The proper expression for the inverse dielectric function is then, in matrix notation

$$\underline{\underline{\varepsilon}}^{-1}(\vec{q},\omega) = [\underline{\underline{\varepsilon}}^{x}(\vec{q},\omega) - \underline{\underline{1}}\,]^{-1} \frac{1}{1-g(\vec{q})} + \underline{\underline{1}} \; . \qquad (5)$$

After adjusting to give a pole in $\varepsilon^{-1}$ at the empirical value of .38eV below the conduction band edge, we find that C=4.98. This is a good deal greater than the value C=1 appropriate to the the interacting electron gas. It is, however, consistent with the result of Hanke and Sham [7], who found that the unadjusted Hubbard exchange factor was too small to give the observed shift toward threshhold in the optical absorption spectrum which was due to the continuum exciton peak.

The calculations for CuCl show that, contrary to the notion that only the lowest conduction bands contribute to $\varepsilon^{-1}$, the higher s-like conduction bands are quite significant. The screened effective interaction

$$V_{sc}(\vec{q},\omega) = \sum_{\vec{G}} \varepsilon^{-1}(\vec{q},\vec{q},+\vec{G};\omega) \; v(q+\vec{G}) \qquad (6)$$

is the important quantity in determining the effect of the dielectric response on the superconducting state. We found that the $\varepsilon^{-1}$ matrix had to include at least 8 shells of reciprocal lattice vectors to get the proper convergence in the $V_{sc}(\vec{q},\omega)$. The sum over $\vec{H}$ in Eq. (2) had to include even more shells. Fortunately, the dependence on $\vec{k}$ and $\vec{q}$ could be neglected for the larger values of $\vec{H}$ or $\vec{G}$ in Eq. (2) and symmetry could be applied to make the summations much more manageable. Also, a much smaller matrix size was possible for calculating $V_{sc}$ accurately for q well within the first Brillouin zone.

An important property for a semiconductor is that it retains a finite value of $\varepsilon(\vec{q},\vec{q},\omega)$ as $q\to 0$. This property is due to the fact that all excitations are between different bands which are mutually orthogonal. Thus as $q\to 0$, the overlap matrix elements in Eq. (4) vanish, whish overcomes the infinite factor $V(q\to 0)$. On the other hand, a metal has intraband transitions so that A(0) does not vanish and $\varepsilon(0,0;0)$ takes on an infinite value which expresses perfect screening. This behavior of $\varepsilon$ for a semiconductor leaves a large postive contribution to $V_{sc}(\vec{q}\to 0,\omega)$ which remains even for frequencies where exciton effects are strong. We can see this in Table II where $V_{sc}$ at the smallest value of $\vec{q}+\vec{G}$ has a large positive value even though it becomes attractive at larger values of $\vec{q}+\vec{G}$. Inkson and Anderson [2] said that this effect should remain even when free carriers were present and that it would destroy any excitonic coupling for a superconductor. Our results indicate

this is not so for CuCl and that the introduction of free carriers drives $V_{sc}$ negative for small q at values just below the exciton threshhold. This result is indicated in Table II.

We have introduced free carriers by assuming that the material is under pressure as was the case in the experimental measurements. We use here the conduction bands of Kunz and Weidman [10] for a contraction to 99% of the lattice constant. The valence bands do not change much, so we retain our equilibrium valence bands. At 99% contraction, the X point becomes nearly degenerate with the $\Gamma_1$ point for the lowest conduction band in [10]. Collins et al [4] have proposed that impurity states in the band gap can pressure-ionize under these conditions and provide free carriers, mostly at the X point. We have used these assumptions in our calculations and do, indeed, find a significant effect at a carrier concentration of $10^{22}cm^{-3}$. The calculations indicate that significantly smaller concentrations will still produce a sizable effect. Note that after introducing free carriers, the

TABLE II. Values of $V_{sc}(\vec{q}+\vec{G},\omega)$ at $\omega$=.09 a.u.

| $\lvert\vec{q}+\vec{G}\rvert$ | Interband only | with free carriers |
|---|---|---|
| .246 | 195. | -9440. |
| .945 | 103. | -640. |
| 1.57 | 45.17 | -198. |
| 1.82 | 39.5 | -148. |
| 1.98 | 11.34 | -89.5 |
| 2.13 | -3.35 | -53.6 |
| 2.28 | -6.98 | -37.0 |

TABLE III. Values of Vsc(q,$\omega$) at fixed q=.246 a.u.

| w(a.u.) | Interband only | with free carriers |
|---|---|---|
| .05 | 210. | 343. |
| .07 | 206. | -70.5 |
| .09 | 195. | -9440. |
| .113 | 352. | |
| .115 | 298. | |
| .15 | | |

values in Table II dip sharply negative at the smallest wavevector. They will approach zero as $q \to 0$.

The values in Table III indicate the expected lowering in value of $V_{sc}$ as $\omega$ approaches the exciton pole at $\omega_{ex}$= .111 a.u. At values just above $\omega_{ex}$, $V_{sc}$ will take on large positive values as shown. Table III shows that although $V_{sc}$ dips in value just below $\omega_{ex}$, it does not go negative. Only when intraband terms are added does a sharp negative dip appear in $V_{sc}$.

Our next step in this study is to make calculations for a wider range of frequencies and free carrier densities. We can also introduce realistic energy bands in a straightforward manner and test other properties of $\varepsilon^{-1}$, such as the optical absorption spectrum. We also plan to study in detail the effect s of non-local exchange. Finally, the same model is being used to study CdS at equilibrium and under pressure.

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# ELECTRONIC STRUCTURE CALCULATION OF WATER ON A COPPER SURFACE*

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Water adsorption on single crystal metal substrates is a subject of current interest with possible electrochemical implications. While in most systems studied to date water clusters have been observed, a recent EELS study of $H_2O$ adsorption on Cu(100)[1] finds monomers at 10°K. This provides the motivation for calculations of the electronic structure of that system since comparisons to the observed vibrational frequencies could provide a check on the theory. In particular such comparisons would provide information on the adequacy of the calculated curvature of the potential energy surface and charge distribution in the system.

We have performed systematic LCAOX$\alpha$[2] cluster calculations of $H_2O$ adsorbed on Cu(100) and compared the properties of a single Cu atom $H_2O$ molecule with those of $H_2O$ adsorbed on larger clusters ($Cu_5H_2O$). We used an extended basis set in these calculations based on atomic basic sets of approximately double-zeta quality found in the literature. To these atomic sets we added extra diffuse functions, polarization functions, and bond-centered functions to handle the effects of molecular bonding. These extra basis functions and, in particular, the polarization functions on O and H significantly affect the cluster binding energies.

At the minimum energy configuration, we find a strong binding energy (3.5eV) for the single Cu atom system with the oxygen bound to the Cu atom and the H-O-H plane oriented at an angle of 57.1° with respect to the Cu-O bond. In addition the H-O-H angle is slightly contracted in comparison to our calculations for free $H_2O$, and the O-H bond length is increased by 35%. The lengths of the bonds and the amount of charge transfer are important in determining the contribution of dynamic dipoles to the vibrations. The Cu d states are not affected much by the Cu-O bond and are rigidly shifted to higher energy, in accordance with UPS studies. For the $Cu_5H_2O$ system the ontop adsorption configuration has the minimum energy separated by small energy barriers from adjacent configurations. We also observe that the H-O-H plane is oriented at an angle to the surface normal and that the binding energy of $H_2O$ is greatly decreased in comparison to the single Cu-$H_2O$ system. We will discuss electronic charge distributions and comparisons to experimental observations.

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